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# Titration microcalorimetry of adsorption processes in aqueous systems

## Interaction of sodium dodecylsulfate and sodium decylsulfate with poly(*N*-vinylpyrrolidone)

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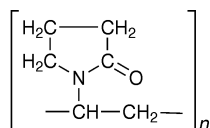
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Procedures are described for analysing enthalpograms characterising adsorption by macromolecules in solution recorded using a titration microcalorimeter. The experimental procedure involves injecting small aliquots of a solution containing adsorbate into a sample cell containing a solution of macromolecular adsorbent. Treatments based on both Langmuir and Frumkin adsorption isotherms are described. The procedures are illustrated by application of the derived equations to the interaction of micelles of sodium dodecylsulfate(aq) and of sodium decylsulfate(aq) with the water-soluble polymer, PVP. The dominant features in the recorded enthalpograms are described using equations developed from the Frumkin equation. In both cases the adsorption is endothermic attributed to hydrophobic interactions between polymer and surfactant. However, an important feature of the analysis is the characterisation of adsorbate-adsorbate interactions using enthalpic interaction parameters. The enthalpograms are characterised by three composition ranges: (i) micelle deaggregation and weak interaction of monomers with polymer, (ii) micelle adsorption on to the soluble polymer up to surface saturation and (iii) micelle dilution.

### Introduction

Understanding the interactions involving macromolecules in aqueous solution offers an interesting and important challenge in view of the importance of these interactions industrially, commercially and biologically. In principle calorimetric techniques offer sensitive procedures for probing these interactions. Thus we have used DSC to probe interactions between surfactant and smaller molecules<sup>1–3</sup> with vesicles in aqueous systems. However, the bilayer structure of vesicles complicates the interpretation. Therefore we have turned our attention to what at first sight appear much simpler systems involving the water-soluble polymer poly(*N*-vinyl pyrrolidone) (PVP) and surfactants, sodium decylsulfate (SDES) and sodium dodecylsulfate (SDS). We have used titration microcalorimetry to study these systems.



In a typical titration microcalorimetric experiment<sup>4,5</sup> small aliquots (typically  $10^{-9} \text{ m}^3$ ) of a given solution containing solute *j* are injected into a sample cell (typically  $10^{-6} \text{ m}^3$ ) containing another solution. The microcalorimeter records the accompanying heat *q* and a plot (enthalpogram) of the ratio  $q/\text{dn}_j^0$  (where  $\text{dn}_j^0$  is the change in the total amount of substance *j* in the sample cell following injection of an aliquot) forms a pattern characteristic of the system when plotted against either injection number or total amount of substance *j* in the sample cell.

The quantitative treatment of the calorimetric data in the case where a solution containing a substrate is injected into a sample cell containing an enzyme(aq) is well established.<sup>6,7</sup> For this case the binding site on the enzyme is well defined

and often specific to a given substrate. Similar comments apply to the calorimetric data describing host-guest interactions.<sup>8</sup> However, this treatment<sup>6</sup> is not appropriate to the analysis titration calorimetric data reported for surfactant-PVP interactions. In developing an appropriate treatment the detailed review by Goddard<sup>9</sup> is particularly informative, highlighting Cabane's model<sup>10</sup> in which the polymer wraps around clusters of the surfactants and which identifies the importance of hydrophobic interactions.<sup>11</sup> The latter class of interactions are also highlighted by Olofsson and Wang<sup>12</sup> with respect to surfactant monomer-polymer interactions. However, as more surfactant is injected in their microcalorimeter experiment, the latter authors argued that surfactant aggregates start to form on the polymer chains,<sup>13</sup> although a quantitative treatment of the enthalpogram was not discussed.

We examine the enthalpograms obtained for polymer-surfactant interactions using an approach based on the Langmuir adsorption isotherm.<sup>14</sup> The derived equations express the measured  $(q/\text{dn}_j^0)$  as a function of an adsorption equilibrium constant, an enthalpy of adsorption  $\Delta_b H^0$  and a quantity  $\pi$  which characterises adsorbate and adsorbent. We calculate the enthalpograms for a number of model situations.

The Langmuir isotherm assumes that there are no adsorbate-adsorbate interactions<sup>15</sup> and that the properties of the solution are ideal. Treatment of the calorimetric data based on the Langmuir adsorption isotherm does not account satisfactorily for the enthalpograms recorded when either SDS(aq) or SDES(aq) is titrated into PVP(aq). Consequently we have examined application of the Frumkin adsorption isotherm taking account adsorbate-adsorbate interactions. The latter include the possibility that the surface, in this case the polymer PVP(aq), changes its organisation following adsorption of surfactant. In fact we show that a key part of the enthalpogram can be accounted for using the Frumkin adsorption isotherm whereby the enthalpy of adsorption depends on the fraction of surface area covered. The most

striking example concerns adsorption of SDS micelles onto PVP where the enthalpy of adsorption per mole of SDS injected switches from endo- to exo-thermic. In this analysis we have assumed that the properties of the surfactant solution are ideal other than in the context of micelle formation. The recorded enthalpograms are nevertheless complicated, indicative of at least three processes which dominate different stages of the titration, micelle deaggregation, micelle dilution and adsorption.

## Experimental

### Materials

PVP, purchased from Acros, had an average relative molar mass of  $4.0 \times 10^4$  u. SDES, purchased from Acros, was of HPLC grade. SDS, purchased from United States Biochemical, was of ultrapure grade.

### Calorimetry

A titration microcalorimeter (Micro Cal Ltd.) was used as previously described.<sup>4</sup> The volume of the sample cell was 1.411 cm<sup>3</sup>. Small aliquots of a solution, volume typically  $5 \times 10^{-6}$  dm<sup>3</sup>, are injected under computer control into the sample cell at pre-defined time intervals. The calorimeter records the difference in rate of heating of sample and reference cells, in order to keep these two cells at a controlled temperature offset while the reference cell (containing water) is slowly heated. The recorded quantity is the rate of heating as a function of time. The individual pulses, separated by a small length of baseline, are integrated to obtain plots recording the ratio of heat  $q$  to the amount of chemical substance  $j$  injected,  $q/dn_j^0$  (see below) as a function of the composition of the sample cell.

### Calculation

The model calculations based on Langmuir and Frumkin adsorption isotherms and the calculations involved in fitting calorimetric results to these isotherms were carried out using TURBO-BASIC computer programs written for a pentium-based PC, linked to printer and plotter peripherals.

### Analysis

In this section we develop a general treatment of titration microcalorimetry which forms the basis of an analysis of enthalpograms of adsorption based on either Langmuir or Frumkin adsorption isotherms.

### Titration microcalorimetry

The enthalpy  $H$  of a closed system can be defined by three independent variables: (i) temperature  $T$ , (ii) pressure  $p$  and (iii) composition,  $\xi$ .

Thus

$$H = H[T, p, \xi] \quad (1)$$

We confine attention to equilibrium states in which the affinity for spontaneous change  $A$  is zero. Hence when the system defined by eqn. (1) is displaced by addition of  $dn_j^0$  moles of chemical substance  $j$ , the displacement is to a neighbouring equilibrium state where the affinity for spontaneous change is also zero. In other words, titration microcalorimetry assumes that the corresponding equilibrium states are thermodynamically stable.<sup>16</sup>

The general differential of eqn. (1) shows that the change in enthalpy  $dH$  as a function of the change in composition is given by eqn. (2).

$$dH = (\partial H / \partial \xi)_{T, p} d\xi \quad (3)$$

Because the change in enthalpy occurs under isobaric conditions, this change is recorded calorimetrically by the heat  $q$ . In

a titration microcalorimeter the system is perturbed by injection of a small amount of chemical substance  $j$ ,  $dn_j^0$ . (We use superscript '0' to identify the change in total amount of substance  $j$  in contrast to the change in equilibrium amount.) Hence eqn. (2) can be written in the following form:

$$q/dn_j^0 = (\partial H / \partial \xi)_{T, p} (d\xi / dn_j^0) \quad (3)$$

Eqn. (3) is fundamental to the technique of titration microcalorimetry. Thus the experimentally important quantity is the ratio of recorded heat  $q$  to the (small) amount of substance  $j$  injected into the sample cell,  $dn_j^0$ . This ratio is recorded for a number, typically around 50, of injections. The problem of data interpretation arises from the fact that the right-hand side of eqn. (3) involves the product of two terms which are unknown 'a priori'.

Thus  $(\partial H / \partial \xi)_{T, p}$  is the enthalpy of reaction, often the target quantity in an experiment. The term  $(d\xi / dn_j^0)$  describes the change in (equilibrium) composition of the solution in the sample cell. In fact a description of the latter solution is required in order to determine  $(d\xi / dn_j^0)$  such that  $(\partial H / \partial \xi)_{T, p}$  follows from measured  $(q/dn_j^0)$ .

In summary we require a chemical model in order to account for the path-dependent macroscopic property,  $q/dn_j^0$ .

In the case of enzyme-substrate interaction,<sup>6,7</sup> an equation for  $(d\xi / dn_j^0)$  is based on a chemical equilibrium describing the binding in terms of a binding equilibrium constant. With reference to ionic surfactants<sup>4,17</sup> the quantity  $(d\xi / dn_j^0)$  describes micelle deaggregation when solutions containing micelles are injected into a solution where the concentration is below the critical micellar concentration. In both types of investigation, the analysis is considerably simplified if the properties of the solutions in sample cell and injected aliquots are ideal in a thermodynamic sense. Hence  $(\partial H / \partial \xi)_{T, p}$  is identified, respectively, as the standard enthalpy of substrate binding<sup>6,7</sup> and the standard enthalpy of micelle deaggregation.<sup>4,17</sup>

### Adsorption from solution

In the experiments reported here, the sample cell contained an adsorbent, PVP(aq), on which chemical substance  $j$ , the adsorbate (e.g. SDS micelles in aqueous solution) were adsorbed. Hence in eqn. (3),  $(\partial H / \partial \xi)_{T, p}$  is the enthalpy of adsorption. In other words, chemical substance  $J$  exists in one of two states, free solute in solution and adsorbed substance:



Then at equilibrium (at fixed  $T$  and  $p$ ) the following condition holds for the equilibrium chemical potentials.

$$\mu_j(\text{aq}) = \mu_j(\text{ads}) \quad (5)$$

A key problem centres on the formulation of  $\mu_j(\text{ads})$  in terms of the fraction of surface area of the adsorbent covered by the adsorbate,  $\theta$ .

### Langmuir adsorption isotherm

**Theory.** Following the proposals by Conway *et al.*<sup>18</sup> and Bockins and Khan,<sup>19</sup> we express  $\mu_j(\text{ads})$  as a function of  $\theta$  using eqn. (6) for a system at fixed temperature and pressure.

$$\mu_j(\text{ads}) = \mu_j^0(\text{ads}) + RT \ln[\theta / (1 - \theta)] \quad (6)$$

We have therefore assumed that there are no adsorbate-adsorbate and no adsorbate-solute interactions. Then  $\mu_j^0(\text{aq})$  is the chemical potential of an ideal adsorbate where  $\theta = 0.5$ , at the same temperature and pressure. In the following analysis we assume that the properties of the solution are ideal;  $\mu_j^0(\text{aq}; c \text{ scale})$  is the chemical potential of solute  $j$  in an ideal solution at unit concentration,  $c_r = c_j = 1 \text{ mol dm}^{-3}$  at the same temperature and pressure. Therefore the equilibrium constant  $K$  characterising the adsorption is given by eqn. (7);

$V$  is the volume of the solution containing  $[n_j^0 - \xi]$  moles of solute  $j$  whereby  $\xi$  moles of solute  $j$  have been adsorbed from solution

$$K = [\theta/(1 - \theta)]Vc_r/(n_j^0 - \xi) \quad (7)$$

If the cross-sectional area of adsorbate is  $a \text{ m}^3 \text{ mol}^{-1}$ , the area covered by the adsorbate is  $\xi a \text{ m}^3$ . If the cross-sectional area of adsorbent available to the adsorbate is  $A \text{ m}^2 \text{ mol}^{-1}$  and if the system in the sample cell contains  $N$  moles of adsorbent, then  $\theta$  equals  $\xi a/NA$ . The system is characterised by  $(a/NA)$ , which we identify as the quantity  $\pi$ , having units  $\text{mol}^{-1}$ ; hence  $\theta = \pi\xi$ . [The form of eqn. (7) requires that in the region of interest (*i.e.* when  $\theta$  changes from greater than to less than 0.5) the magnitude of  $\pi$  is similar to  $\xi$ , the extent of adsorption of the adsorbate.] In these terms, eqn. (7) can be written in the form of an equation involving the extent of adsorption,  $\xi$ .

Thus

$$K = [\pi\xi/(1 - \pi\xi)]Vc_r/(n_j^0 - \xi) \quad (8)$$

By definition

$$q = (K/Vc_r)^{-1} \quad (9)$$

Then

$$q\pi\xi = (1 - \pi\xi)(n_j^0 - \xi) \quad (10)$$

Hence

$$\pi\xi^2 - \xi(1 + \pi n_j^0 + q\pi) + n_j^0 = 0 \quad (11)$$

Granted estimates of parameters  $\pi$  and  $K$ , extent of adsorption  $\xi$  is related by a quadratic to the total amount of surfactant in the sample cell. Further, as indicated by the key eqn. (3), we require  $(d\xi/dn_j^0)$ . Then from eqn. (10),

$$(d\xi/dn_j^0) = (1 - \pi\xi)/[q\pi + \pi(n_j^0 - \xi) + (1/\pi\xi)] \quad (12)$$

It turns out that only one root of the quadratic is physically significant and so through eqn. (12),  $(d\xi/dn_j^0)$  is obtained for each solution across the set of titrations in a titration calorimetric experiment.

The enthalpy term  $(\partial H/\partial \xi)_{T,p}$  in eqn. (3) is problematic. Application of the Gibbs–Helmholtz equation to eqn. (6) shows that the partial molar enthalpy of the adsorbate is a function of the reference partial molar enthalpy (where  $\theta = 0.5$ ),  $H_j^0(\text{ads})$ ,  $\theta$  and the dependence of  $\theta$  on temperature. In the absence of information concerning  $d \ln \theta/dT$  we set  $H_j^0(\text{ads})$  equal to  $H_j(\text{ads})$ , independent of  $\theta$ . Also assuming the properties of the solution containing  $j$  are ideal we set  $H_j(\text{aq}) = H_j^\circ(\text{aq})$ ; (see below). The enthalpy of the solution in the sample cell is given by eqn. (13). In effect we have assumed  $(d\theta/dT)$  is zero at all  $\theta$  values.

$$H(\text{sample cell}) = n_1 H_1^*(\ell) + (n_j^0 - \xi) H_j^0(\text{aq}) + \xi H_j^0(\text{ads}) + H(\text{polymer}) \quad (13)$$

Here  $H_1^*(\ell)$  is the molar enthalpy of pure water at the same temperature and pressure;  $H(\text{polymer})$  is the enthalpy of the polymer in solution referring to the contribution to the enthalpy of the system other than that from the adsorbate on the polymer.

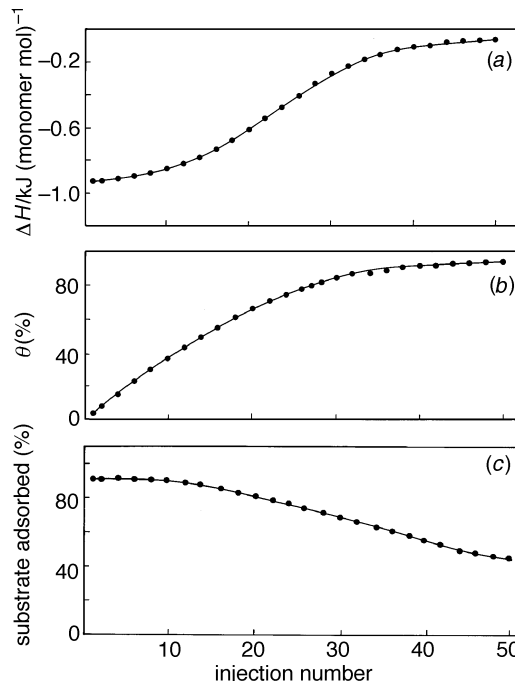
Then the partial derivative  $(\partial H/\partial \xi)_{T,p}$  required in eqn. (3) is given by

$$(\partial H/\partial \xi)_{T,p} = \Delta_{\text{ad}} H^0 = H_j^0(\text{ads}) - H_j^0(\text{aq}) \quad (14)$$

Hence using a given equilibrium constant  $K$ , the parameter  $\pi$  and  $\Delta_{\text{ad}} H^0$ , we can obtain  $q/dn_j^0$  as a function of the composition of the sample cell or, equivalently, the injection number.

### Results of computer-based calculations

Eqn. (11), (12) and (14) were used in conjunction with eqn. (3) to predict the shape of an enthalpogram required by the



**Fig. 1** Langmuir adsorption isotherm; volume of sample cell =  $1.4 \text{ cm}^3$ ; volume of injected aliquot =  $1.0 \times 10^{-6} \text{ dm}^3$ ;  $\Delta_{\text{ad}} H^0 = 10 \text{ kJ mol}^{-1}$ ;  $\pi = 5.0 \times 10^4 \text{ mol}^{-1}$ ; concentration of adsorbent in sample cell =  $1.42 \times 10^{-2} \text{ mol dm}^{-3}$ ; adsorption equilibrium constant =  $1.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ ; amount of adsorbate in each injection =  $8.0 \times 10^{-7} \text{ mol}^{-1}$ ;  $T = 298.2 \text{ K}$ ; the identified points are calculated. Dependences on injection number of (a) enthalpy of adsorption,  $\Delta_{\text{ad}} H$ , (b) fraction of surface area of adsorbent covered by adsorbate,  $\theta$  and (c) fraction of surface area of adsorbent covered by adsorbate at each stage of the series of injected aliquots.

Langmuir adsorption isotherm. A typical result of these calculations is shown in Fig. 1 based on the assumption that the standard enthalpy of adsorption is  $-10 \text{ kJ mol}^{-1}$ . The calculated enthalpy of adsorption [Fig. 1(a)] forms a sigmoidal dependence as a function of injection number. This enthalpy changes gradually until the percentage of the surface covered approaches 70% [Fig. 1(b)]. As  $\theta$  gradually approaches 100%, the exothermic enthalpy of adsorption decreases and approaches zero. The pattern summarised in Fig. 1(c) shows that over the first 20 injections more than 80% of the injected adsorbate is adsorbed by the adsorbent. With increase in number of injections so the trend is towards a situation where only 50% of the injected adsorbate is adsorbed. The patterns summarised in Fig. 1, particularly the pattern of the calculated enthalpograms, provide a benchmark against which to compare measured enthalpograms.

### Frumkin adsorption isotherm

**Theory.** The Frumkin adsorption isotherm recognises the possibility that there are adsorbate–adsorbate interactions which are determined by the extent of surface coverage. Then [cf. eqn. (6)]

$$\mu_j(\text{ads}) = \mu_j^0(\text{ads}) + RT \ln [\theta/(1 - \theta)] - RT\phi\theta \quad (15)$$

Thus quantity ‘ $\phi$ ’ determines the extent to which the chemical potential of the adsorbate in the real system differs from that in the corresponding ideal system.

As described above we express the degree of surface coverage  $\theta$  by the product  $\pi\xi$ . Then eqn. (16) is the Frumkin analogue of eqn. (8).

Thus

$$K = [\pi\xi/(1 - \pi\xi)] \exp(-\phi\pi\xi) [Vc_r/(n_j^0 - \xi)] \quad (16)$$

Unfortunately this equation is not readily solved for  $\xi$  granted estimates of  $K$ ,  $\pi$ ,  $\phi$ ,  $V$  and  $n_j^0$ . In the computer analysis (see below) we defined two terms;  $F_1$  and  $F_2$ .

$$F_1 = (K/V)(1/c_r)(n_j^0 - \xi) \quad (17)$$

$$F_2 = [\pi\xi/(1 - \pi\xi)]\exp(-\phi\pi\xi) \quad (18)$$

Then  $\xi$  was gradually incremented and the arithmetic solution was identified where  $(F_1 - F_2)$  is zero. Then with  $\gamma$  defined by  $(Vc_r/K)$ , the derivative required by eqn. (3) is obtained.

$$d\xi/dn_j^0 = (1/\pi\xi)/\beta \quad (19)$$

where

$$\beta = [\pi\gamma \exp(-\phi\pi\xi)](1 - \phi\pi\xi) - (2\pi\xi - 1 - \pi n_j^0) \quad (20)$$

In the computer-based calculation associated with eqn. (17) and (18), the increments on estimated  $\xi$  must be small in seeking the arithmetic solution of  $\xi$ ; the differential quantity  $(d\xi/dn_j^0)$  in eqn. (19) and (20) is particularly sensitive to the precision in the estimated  $\xi$ .

The Gibbs-Helmholtz equation in conjunction with eqn. (15) yields an even more complicated equation for the partial molar enthalpy of the adsorbate  $H_j(\text{ads})$  than obtained using the Langmuir adsorption isotherm. In any event,  $H_j(\text{ads})$  is a function of  $\theta$  and an adsorbate-adsorbate enthalpic interaction parameter. Therefore, we have assumed that  $H_j(\text{ads})$  is related to  $\theta$  via eqn. (21). Thus in terms of apparent molar enthalpies,  $\phi[H_j(\text{ads})]$ ,

$$\phi[H_j(\text{ads})] = H_j^0(\text{ads}) + h_{jj}\theta \quad (21)$$

Assuming that the properties of the solution are ideal, the enthalpy of the solution in the sample cell is given by the analogue of eqn. (13);

$$H(\text{sample cell}) = n_1 H_1^*(\ell) + (n_j - \xi)H_j^0(\text{aq}) + \xi[H_j^0(\text{aq}) + h_{jj}\pi\xi] - H(\text{polymer}) \quad (22)$$

Then the partial derivative  $(\partial H/\partial \xi)_{T,p}$  in eqn. (3) is given by

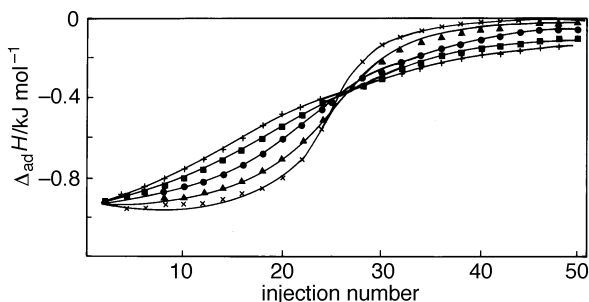
$$(\partial H/\partial \xi)_{T,p} = \Delta_{\text{ads}} H^0 + 2h_{jj}\theta \quad (23)$$

We have explored two cases with respect to the Frumkin adsorption isotherm.

**Case I.** Granted an equilibrium constant  $K$  and parameter  $\pi$ , we have probed the impact of the Frumkin  $\phi$  parameter in eqn. (15) on the calculated dependences of  $q/dn_j^0$ ,  $\theta$  and percentage adsorbed on injection number [cf. eqn. (16), (19) and (20)] for a defined  $\Delta_{\text{ads}} H^0$ , where  $h_{jj}$  is zero.

### Results of computer-based calculations

The essential results of the calculations are illustrated by the five enthalpograms in Fig. 2. The curve describing the calcu-

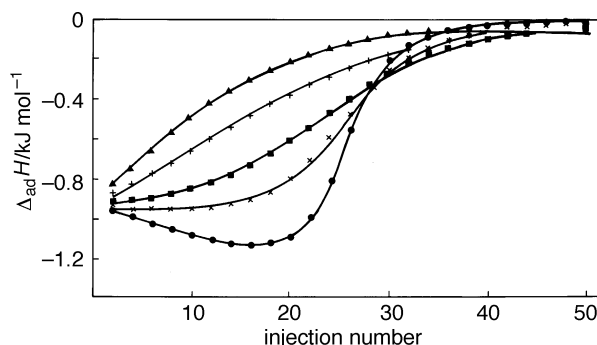


**Fig. 2** Calculated enthalpograms based on the Frumkin adsorption isotherm. The system parameters are as described in the caption to Fig. 1 except that the Frumkin adsorbate-adsorbate interaction parameter,  $\phi$  defined in eqn. (15) is  $\phi = 2.0$  ( $\times$ );  $\phi = 1.0$  ( $\Delta$ );  $\phi = 0.0$  ( $\circ$ ); i.e. Langmuir;  $\phi = -1$  ( $\square$ );  $\phi = -2$ ; in all cases  $h_{jj} = 0$ .

lated enthalpogram where ' $\phi = 0.0$ ' is a useful reference; identifying the corresponding Langmuir adsorption isotherm. For systems where  $\phi > 0.0$ , eqn. (15) shows that (in the absence of other contributions) the chemical potential of the adsorbate is below that for the ideal case and so over the first set of injections the enthalpogram records more exothermic injections than in the Langmuir case. Thus adsorption is favoured, but this pattern means that the coverage of the surface is higher. Hence at high injection number the exothermic enthalpy of adsorption is less than in the Langmuir case. For systems where  $\phi < 0.0$ , the chemical potential of the adsorbate is higher than for an ideal adsorbate. Consequently over the first set of injections the exothermic adsorption is less dramatic than in the Langmuir case. Therefore the percentage of the surface covered is less. Hence at high injection numbers the adsorption is more exothermic than in the ideal case. Comparison of the enthalpograms (Fig. 2) for cases where the  $a$  parameter changes from above to below zero, shows a switch in pattern about injection number 25, where the fraction of surface covered is in the region of 50%.

**Case II.** The calculation in case I was repeated except the impact of both positive and negative enthalpic interaction parameters [cf. eqn. (23)] was examined. Enthalpic interaction parameters were chosen to enhance the patterns obtained, in Fig. 2 where the non-ideal component was confined to the chemical potential of the adsorbate. In describing the patterns in Fig. 3, the Langmuir adsorption enthalpogram is again a convenient reference point. The positive  $\phi$  parameter and negative  $h_{jj}$  combine to form a pattern where the exothermicity increases over the first set of injections but as described in conjunction with Fig. 2, the enthalpy of adsorption for each injection becomes less marked at low injection numbers. The patterns in Fig. 3 hint at the complexity which can emerge for real systems as a consequence of the non-ideal properties of the adsorbate. This comment forms the link with the results for two real systems described below.

**Aqueous solutions containing SDES and SDS.** As reference points, a series of enthalpograms were recorded in which the sample cell at the start of each experiment contained only water and the syringe contained one of the cited ionic surfactants at a concentration above the quoted<sup>20</sup> c.m.c. Thus the compilation by van Os *et al.*<sup>20</sup> states that for aqueous solutions at 298.2 K (a) c.m.c. (SDS) =  $7.24 \times 10^{-3}$  mol dm<sup>-3</sup> with (calorimetrically)  $\Delta_{\text{mic}} H^\infty(\text{aq}) = 0.1$  kJ mol<sup>-1</sup>, and (b) c.m.c. (SDES) =  $33 \times 10^{-3}$  mol dm<sup>-3</sup> with (calorimetrically)  $\Delta_{\text{mic}} H^\infty = 2.1$  kJ mol<sup>-1</sup>. Previously<sup>4</sup> we reported that in the case of CTAB(aq) a sharp break in the enthalpogram occurs at the c.m.c. leading to satisfactory estimates of both c.m.c.

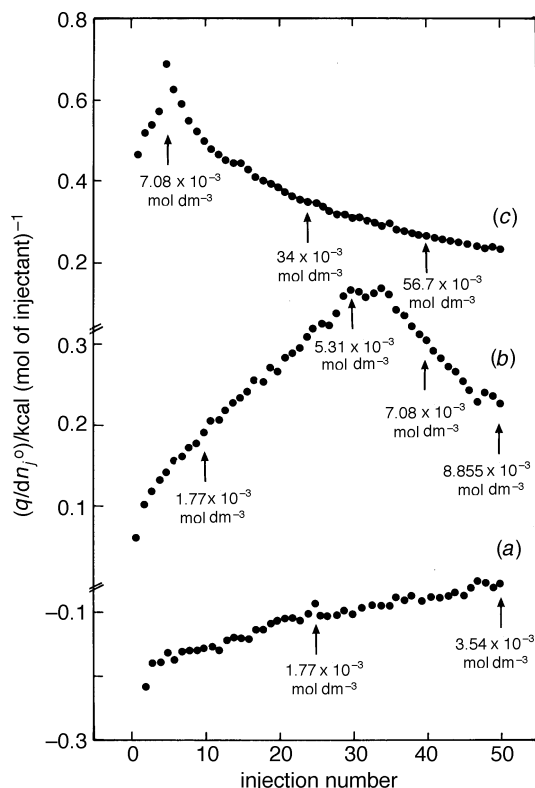


**Fig. 3** Calculated enthalpogram based on the Frumkin adsorption isotherm. The system parameters are as described in the caption to Fig. 1 except that the Frumkin  $a$  parameter (Fig. 2) and enthalpic adsorbate-adsorbate interaction parameters [eqn. (15) and (23)]  $h_{jj}$  are given by:  $\phi = +2.0$  and  $h_{jj} = -5.0$  kJ mol<sup>-1</sup> ( $\circ$ );  $\phi = +1.0$  and  $h_{jj} = -2.0$  kJ mol<sup>-1</sup> ( $\times$ );  $\phi = 0.0$  and  $h_{jj} = 0.0$  ( $\square$ );  $\phi = -1.0$  and  $h_{jj} = +5.0$  kJ mol<sup>-1</sup> ( $+$ ) and  $\phi = -2.0$  and  $h_{jj} = 10.0$  kJ mol<sup>-1</sup> ( $\Delta$ ).

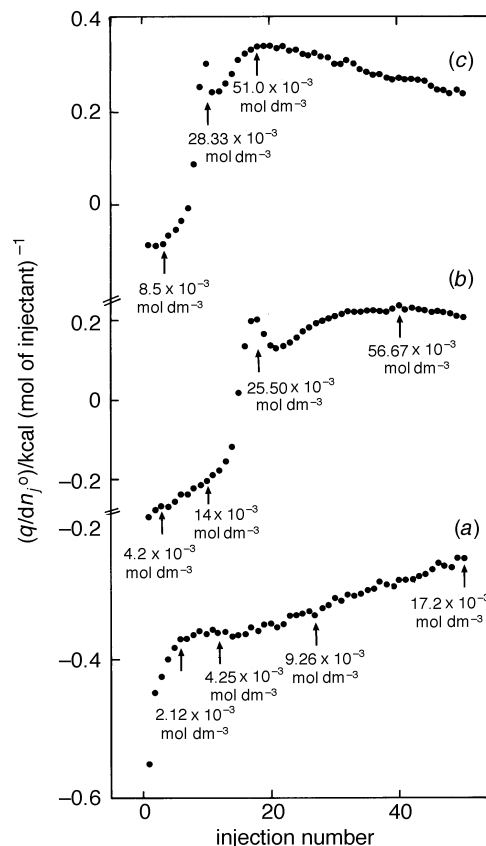
and  $\Delta_{\text{mic}} H^\infty$ . Surfactant systems which are characterised by similar shaped enthalpograms were classified<sup>17</sup> as Type A. However, in other cases the enthalpograms are less clear cut. In Type B the plots of  $(q/dn_j^0)$  against injection number pass through a maximum; e.g. 4-dodecyl-1-methylpyridinium methylsulfate.<sup>17,21</sup> The shape of the plot is accounted for in terms of micelle deaggregation and in terms of the fact that both syringe and sample contain moderately concentrated salt solutions. Moreover, as the titration proceeds so the composition of sample cell changes. Hence the extent to which the properties of the solution in the sample cell deviate from ideal also changes. The extent to which the composition of the sample cell corresponding to the maximum in  $(q/dn_j^0)$  can be precisely identified as the c.m.c. is therefore open to question. Therefore analysis of the recorded Type B enthalpograms is less certain.

### Calorimetric results

The enthalpograms recorded for solutions containing SDS(aq) and SDES(aq) are shown in Fig. 4 and 5. The patterns in Fig. 4 and 5 show an initial gradual increase in  $(q/dn_j^0)$ ; in both cases the concentration of surfactants in the sample cells are below their c.m.c.s. In both cases [Fig. 4(a) and Fig. 5(a)] dilution of the surfactants from above to below the c.m.c.s is endothermic but becomes less endothermic with increasing injection number. With increasing surfactant concentration in each aliquot, the concentration of surfactant in the sample cell passes the c.m.c.s given above; Fig. 4(b) and 5(b). When the syringe contains SDS(aq;  $50 \times 10^{-3} \text{ mol dm}^{-3}$ ) or SDES(aq;  $400 \times 10^{-3} \text{ mol dm}^{-3}$ ), the enthalpograms become more endothermic with increasing injection number passing through maxima near  $6 \times 10^{-3} \text{ mol dm}^{-3}$  for SDS(aq), Fig. 4(b) and (c) and near  $26.0 \times 10^{-3}$  for SDES(aq), [Fig. 5(b) and (c)] which is slightly lower than the literature values.<sup>20</sup>



**Fig. 4** Enthalpogram recorded for dilution of SDS(aq) into a sample cell initially containing water;  $T = 298.2 \text{ K}$ ; injected aliquot =  $5.0 \times 10^{-6} \text{ dm}^3$ ; volume of sample cell =  $1.411 \text{ cm}^3$ ; concentration of SDS (monomer) in each injected aliquot = (a)  $20.0 \times 10^{-3}$ , (b)  $50.0 \times 10^{-3}$  and (c)  $400 \times 10^{-3} \text{ mol dm}^{-3}$ . Plots are annotated to show SDS concentration in the sample cell.



**Fig. 5** Enthalpograms recorded for dilution of SDES(aq) into a sample cell initially containing water;  $T = 298.2 \text{ K}$ ; injected aliquot =  $5 \times 10^{-6} \text{ dm}^3$ ; volume of sample cell =  $1.411 \text{ cm}^3$ ; concentration of SDES (monomer) in each injected aliquot = (a)  $100 \times 10^{-3} \text{ mol dm}^{-3}$ , (b)  $400 \times 10^{-3} \text{ mol dm}^{-3}$  (c)  $800 \times 10^{-3} \text{ mol dm}^{-3}$

With increasing surfactant concentration to SDS(aq;  $400 \times 10^{-3} \text{ mol dm}^{-3}$ ) and SDES(aq;  $100 \times 10^{-3} \text{ mol dm}^{-3}$ ), in the injected aliquot, the enthalpograms are endothermic, passing through maxima and then decreasing with increase in injection number; Fig. 4(c) and 5(c). The endothermic maxima occur at  $7.08 \times 10^{-3} \text{ mol dm}^{-3}$  SDS(aq) and at  $25.50 \times 10^{-3} \text{ mol dm}^{-3}$  for SDES(aq).

The estimate of the c.m.c. for SDS(aq) obtained from Fig. 4(c) is encouragingly close to the published estimates, the estimates in ref. 24 indicating between  $7.2$  and  $8.2 \times 10^{-3} \text{ mol dm}^{-3}$ . The estimate of the c.m.c. for SDES(aq) obtained from Fig. 4(c) is slightly lower than most estimates in ref. 20 which are around  $33 \times 10^{-3} \text{ mol dm}^{-3}$ . This slight disagreement is probably a consequence of the fact that no correction has been made here for the non-ideal properties of the solution.<sup>17</sup>

For the systems described in Fig. 4(c) and 5(c) we draw attention to the gradual decrease in  $(q/dn_j^0)$  with injection number when the concentrations of surfactants far exceeds the c.m.c. We return to this point below.

### Aqueous solutions containing either SDS or SDES injected into PVP(aq)

The previous section reported experiments which form the background to the key set of enthalpograms when the sample cell contained PVP(aq); Fig. 6 and 7. As before, the experiments involved a series of experiments with gradually increasing concentration of surfactant in the injected aliquots.

The recorded pulses in the titration experiments characterising the sequence of injections were well-separated, showing that the time constants characterising the adsorption processes are short compared with the time constants for the calorimeter.<sup>22</sup> The experiments using SDS(aq) set the pattern;

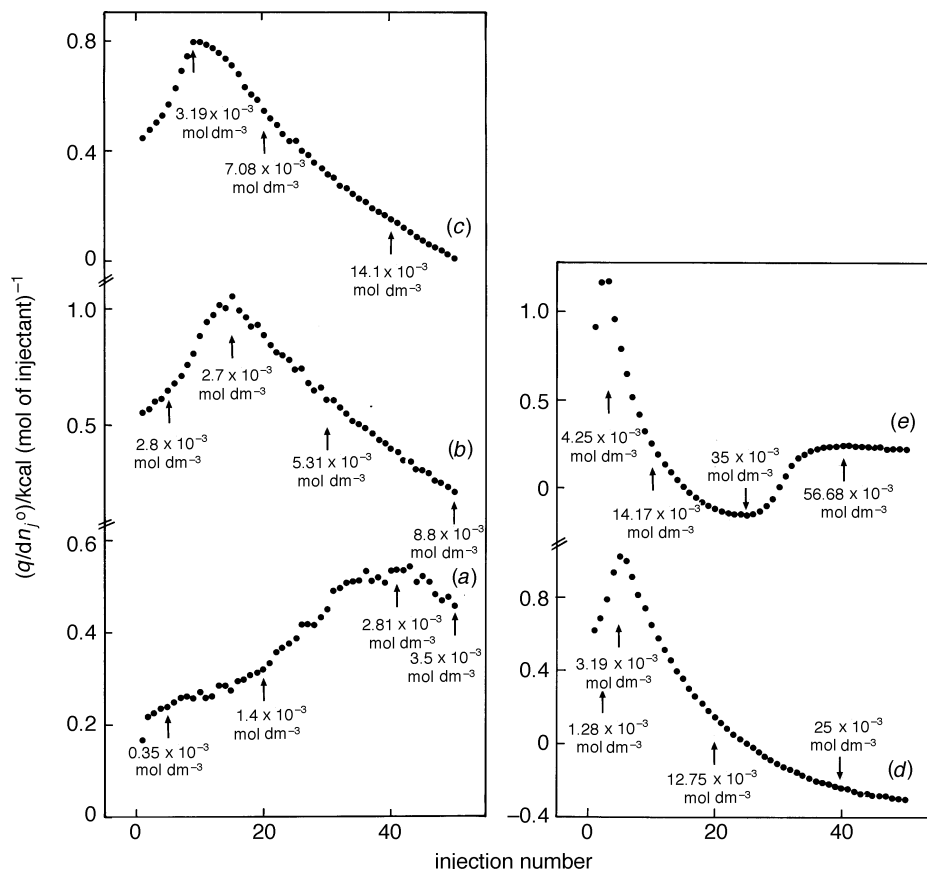


Fig. 6 Comparison of enthalpograms recorded for the injection of SDS(aq:  $5 \times 10^{-6} \text{ dm}^3$ ) into PVP(aq: 1%:  $1.4116 \text{ cm}^3$ ) at 298.2 K when the concentration of SDS in injected aliquot is (a)  $20 \times 10^{-3} \text{ mol dm}^{-3}$ , (b)  $50 \times 10^{-3} \text{ mol dm}^{-3}$ , (c)  $100 \times 10^{-3} \text{ mol dm}^{-3}$  (d)  $180 \times 10^{-3} \text{ mol dm}^{-3}$  and (e)  $400 \times 10^{-3} \text{ mol dm}^{-3}$

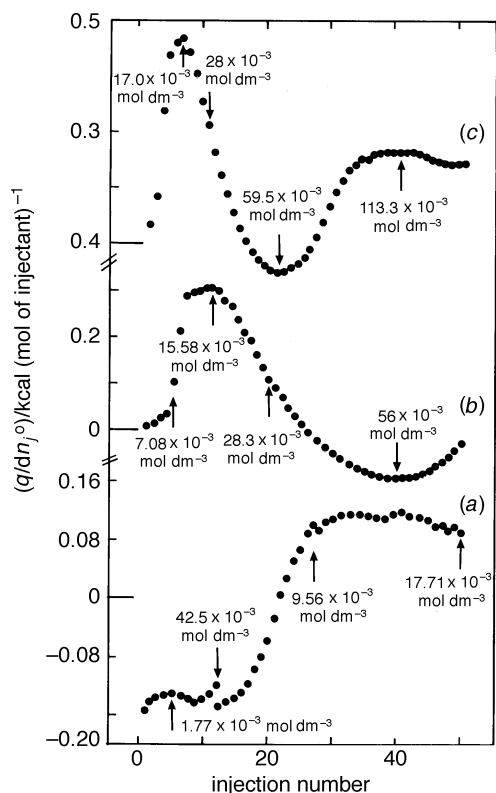
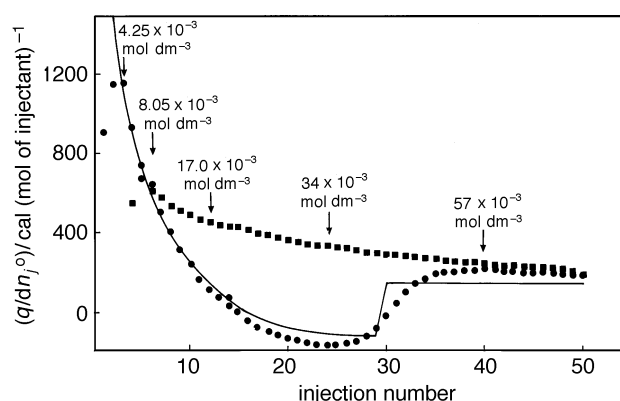


Fig. 7 Comparison of enthalpograms recorded for the injection of SDES(aq:  $5 \times 10^{-6} \text{ dm}^3$ ) into PVP(aq: 1%:  $1.4116 \text{ cm}^3$ ) at 298.2 K where the concentration of SDES in injected aliquot is (a)  $100 \times 10^{-3} \text{ mol dm}^{-3}$ , (b)  $400 \times 10^{-3} \text{ mol dm}^{-3}$  and (c)  $800 \text{ mol dm}^{-3}$

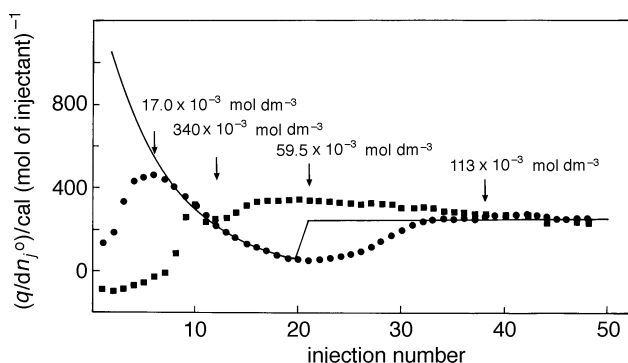
Fig. 6. At the lower concentration of SDS(aq),  $50 \times 10^{-3} \text{ mol dm}^{-3}$  with PVP(aq: 1%) in the sample cell, the enthalpogram [Fig. 6(a)] records endothermic injections, with an endothermic maximum at a concentration near  $3.00 \times 10^{-3} \text{ mol dm}^{-3}$ , clearly below the c.m.c. for SDS(aq) in the absence of PVP. With increase in concentration of SDS(aq) in the injected aliquot [Fig. 6(b)], the endothermic maximum is slightly sharper but at approximately the same concentration. With increase in SDS(aq) concentration in each SDS aliquot, this pattern continues. Interestingly for those systems where the concentration of SDS(aq) equals  $400 \times 10^{-3} \text{ mol dm}^{-3}$ , the endothermic maximum is sharply defined and at the same concentration. (The resolution of the c.m.c. decreases with increase of surfactant concentration where the aim was to record the enthalpogram across a wide range of SDS concentrations in the sample cell and in the presence of PVP.) However, the enthalpograms change to exothermic at higher SDS concentrations. Eventually at much higher injection numbers these enthalpograms move to endothermic,  $(q/dn_j^0)$  becoming effectively independent of injection number.

The pattern followed by the SDES(aq) systems is broadly similar; Fig. 7. At the lowest SDES concentration [Fig. 7(a)], the first set of injections are exothermic, becoming endothermic at higher SDES(aq) concentrations. With increasing SDES concentration the endothermic extremum remains approximately constant [Fig. 7(b) and 7(c)]. A change from endothermic to exothermic is observed in Fig. 7(b) but at higher SDES concentrations [Fig. 7(c)] this is not observed, although  $(q/dn_j^0)$  values over a short span of injection are close to athermal. However, as in the case of SDS, the injections approached a constant endothermic value at high injection numbers.

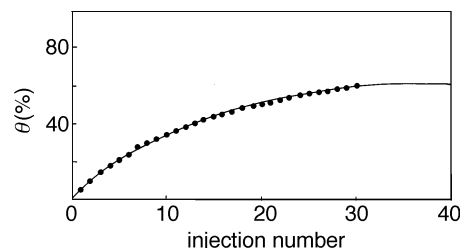
**Analysis.** In the context of the experimental results reported here, Fig. 8 and 9 form the core of the argument. In each figure we compare enthalpograms recorded for injection of anionic surfactant at the same concentration into a sample cell containing initially either water or PVP(aq). For SDS the initial endothermic maximum is more marked when PVP is present in the sample cell. The enthalpogram when PVP is present shows a marked change in  $(q/dn_j^0)$ , becoming exothermic at higher injection numbers. Interestingly the enthalpogram then switches to endothermic. Significantly the plot follows the enthalpogram recorded in the absence of PVP. In these terms, the enthalpogram breaks into roughly three domains. At low injection numbers (*i.e.* 1–6), the data points show increasing endothermic injections. The data points at injection numbers from 6 to *ca.* 25, fall on a smooth curve. In the last set and significantly the data points switch back to follow the points marking simple surfactant dilution, injection numbers 40–50. In fact, the data points over the range 6–25 are satisfactorily accounted for using the Frumkin adsorption isotherm up to around 60% surface coverage (Fig. 10). This percentage marks an upper limit. In the calculations we stopped the fitting procedures at a given injection number, arbitrarily setting  $(q/dn_j^0)$  over the remaining set of injections to fixed value in order to coincide with the experimental  $(q/dn_j^0)$ . The calculated curves in effect stops at this point but in Fig. 8 and 9 we have linked the two plots to emphasise the



**Fig. 8** Comparison of enthalpograms recorded for injection of aliquots of SDS(aq:  $400 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $5 \times 10^{-6} \text{ dm}^{-3}$ ) into a sample cell ( $1.411 \text{ cm}^3$ ) containing initially (a) water (■) and (b) PVP(aq: 1%) (●). Comparison with enthalpogram calculated using Frumkin adsorption isotherm; eqn. (16), (19) and (23) with  $K = 40.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ ,  $\phi = -0.2$ ,  $\pi = 2.83 \times 10^6 \text{ mol}^{-1}$ ,  $\Delta_{\text{ads}}H^0 = -250 \times 10^3 \text{ cal mol}^{-1}$  and  $h_{jj} = -560 \times 10^{-3} \text{ cal mol}^{-1}$ .



**Fig. 9** Comparison of enthalpograms recorded for injection of aliquots of SDES (aq:  $800 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $5 \times 10^{-6} \text{ dm}^{-3}$ ) into a sample cell containing initially (a) water (■) and (b) PVP(aq: 1%) (●). Comparison with enthalpogram calculated using Frumkin adsorption isotherm; eqn. (16), (19) and (23) with  $\phi = 9.0 \times 10^{-2} \text{ mol}^{-1}$ ,  $K = 20.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ ,  $\pi = 2.83 \times 10^6$ ,  $\Delta_{\text{ads}}H^0 = 450 \times 10^3 \text{ cal mol}^{-1}$ ,  $h_{jj} = -450 \times 10^{-3} \text{ cal mol}^{-1}$ .



**Fig. 10** Fraction of surface area of PVP(aq) covered by SDS(aq) for the system described in Fig. 8; data points calculated using the parameters given in the caption to Fig. 8

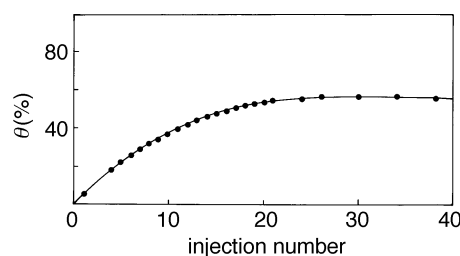
change in pattern.

The pattern for systems involving SDES is very similar (Fig. 9), the Frumkin adsorption isotherm accounting satisfactorily for the pattern over the middle group of injections. The calculations indicate that the percentage of surface covered reaches a maximum of around 50% (Fig. 11).

## Discussion

The enthalpograms summarised in Fig. 8 and 9 clearly identify three distinct regions. In fact several published reports<sup>9,12,13,22–24</sup> identify the three regions, although explanations differ in detail. Possibly most disagreement centres on explanations of the enthalpogram at SDS and SDES concentrations below the concentrations corresponding to the endothermic maxima. Those extrema occur at the critical aggregation concentration (c.a.c.), which is usually below the c.m.c. of the surfactant. This shift and the fact that below the c.a.c.  $(q/dn_j^0)$  is more endothermic points to surfactant–PVP interactions. We account for these observations in terms of micelle deaggregation when each aliquot is injected where a proportion of the SDS (or SDES) exists as free sodium ions and surfactant anions. However, a proportion of the surfactant monomers in the sample cell associate with the PVP, this process being driven by hydrophobic interaction and hence producing a stronger endothermicity than in the absence of PVP. The monomers continue to be adsorbed and the concentration of free monomers in the solution remains almost constant as more surfactant is injected. A possible contribution to the initial endothermicity may also arise from PVP–SDS monomer competition for hydrating water molecules.

At the c.a.c., the injected micelles are adsorbed on to the polymer chain. This association is again driven by hydrophobic interactions involving three methylene groups of the surfactant anion (near the charged headgroup) and the hydrophobic domains of the polymer. This adsorption continues until the polymer is saturated at a second critical concentration, *c*<sub>2</sub> where SDS the polymer/surfactant ratio is 2.65. The latter estimate is comparable to the ratio calculated using other techniques<sup>13</sup> when the polymer is polyethylene glycol;



**Fig. 11** Fraction of surface area of PVP(aq) covered by SDES(aq) for the system described in Fig. 9; data points calculated using the parameters given in the caption to Fig. 9



e.g. 2.3 from heat capacities<sup>13</sup> and 2.8 from enthalpies.<sup>12</sup> For SDES we obtain a ratio of 1.5.

The absorption follows a pattern described by the Frumkin isotherm in which an important feature is the dependence of the enthalpy of adsorption on surface coverage. The ideal term is again endothermic, consistent with hydrophobic interaction between surfactant and polymer. However, the non-ideal component is indicative of a strong co-operativity of the interactions along the polymer chain. In fact this feature is sufficient in the case of SDS to produce exothermic adsorption at high surface coverages and almost sufficient in the case of SDES to change the sign of  $(q/dn_j^0)$ . It is not possible to formulate a model for the system solely on the basis of this thermodynamic information, but the string of beads model in which the polymer wraps around the surfactant is not out-of-line with this co-operativity. The pattern is also supported by the limiting surface occupancy such that where excess surfactant is injected the enthalpogram tracks the pattern formed by dilution of micelles from the syringe into the sample cell (Fig. 8 and 9). Indeed, if insufficient surfactant is injected into the sample, the recorded enthalpograms show that the corresponding plot of  $(q/dn_j^0)$  for systems containing PVP do not rejoin the recording enthalpogram recorded in the absence of PVP. In other words the polymer surface is not saturated at the higher injection number.

In conclusion we have shown that the Frumkin adsorption isotherm provides a satisfactory basis for analysing the enthalpograms recorded using a titration microcalorimeter for the absorption of surfactants on a soluble polymer in aqueous solution.

## References

- 1 M. J. Blandamer, B. Briggs, P. M. Cullis, J. B. F. N. Engberts and A. Kacperska, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 4275.
- 2 M. J. Blandamer, B. Briggs, M. D. Butt, M. Waters, P. M. Cullis, J. B. F. N. Engberts, D. Hoekstra and R. K. Mohanty, *Langmuir*, 1994, **10**, 3488.
- 3 M. J. Blandamer, B. Briggs, P. M. Cullis, J. B. F. N. Engberts and D. Hoekstra, *Thermochim. Acta*, 1994, **247**, 341.
- 4 J. Bach, M. J. Blandamer, J. Burgess, P. M. Cullis, L. G. Soldi, K. Bijma, J. B. F. N. Engberts, P. A. Kooreman, A. Kacperska, K. C. Rao and M. C. S. Subha, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1229.
- 5 J. Kevelam, J. F. L. van Breemen, W. Blokzijl and J. B. F. N. Engberts, *Langmuir*, 1996, **12**, 4709.
- 6 T. Wiseman, S. Williston, J. F. Brandts and L. N. Lin, *Anal. Biochem.*, 1989, **179**, 131.
- 7 J. E. Ladbury and B. Z. Chowdhry, *Chem. Biol.*, 1996, **3**, 791.
- 8 V. Rüdiger, A. Eliseer, S. Simova, H.-J. Schneider, M. J. Blandamer, P. M. Cullis and A. J. Meyer, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2119.
- 9 E. D. Goddard, *J. Am. Oil Chem. Soc.*, 1994, **71**, 1.
- 10 B. Cabane, *J. Phys. Chem.*, 1977, **81**, 1639.
- 11 W. Blokzijl and J. B. F. N. Engberts, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 5145.
- 12 G. Olofsson and G. Wang, *Pure Appl. Chem.*, 1994, **66**, 527.
- 13 See also K. Ballerat-Busserolles, G. Roux-Desgranges and A. H. Roux, *Langmuir*, 1997, **13**, 1946.
- 14 I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1361.
- 15 K. S. Pitzer, *Thermodynamics*, McGraw-Hill, New York, 3rd edn., 1995, ch. 23.
- 16 I. Prigogine and R. Defay, *Chemical Thermodynamics*, transl. D. H. Everett, Longmans Green, London, 1954.
- 17 K. Bijma, J. B. F. N. Engberts, M. J. Blandamer, P. M. Cullis, P. M. Last, K. D. Irlam and L. G. Soldi, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 1579.
- 18 B. E. Conway, H. Angerstein-Kozłowska and H. P. Dhar, *Electrochim. Acta*, 1975, **19**, 189.
- 19 J. O'M. Bockris and S. U. M. Khan, *Surface Electrochemistry*, Plenum Press, New York, 1993.
- 20 N. M. van Os, J. R. Haak and L. A. M. Rupert, *Physico-Chemical Properties of Selected Anionic, Cationic and Non-Ionic Surfactants*, Elsevier, Amsterdam, 1993.
- 21 K. Bijma, PhD Thesis, University of Groningen, The Netherlands, 1995.
- 22 D. M. Bloor and E. Wyn-Jones, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 657, and references therein.
- 23 M. L. Fishman and F. R. Eirich, *J. Phys. Chem.*, 1971, **75**, 3135; 1975, **79**, 2740.
- 24 F. M. Witte and J. B. F. N. Engberts, *J. Org. Chem.*, 1987, **52**, 4767.

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